Environmental Exposure to Chromium Compounds in the Valley of León, México

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The effects on the environment and health of the operation of a chromate compounds factory and tanneries in the León valley in central México are discussed. Sampling and analysis of chromium were performed in water, soil, and human urine. Groundwater has been polluted in an area of about 5 km^2 by the leaching of a solid factory waste, which results in concentrations up to 50 mg/l of hexavalent chromium. The plume shape and extension appear to be controlled by the prevailing well extraction regime. Total chromium was detected in the soil around the factory as a result of both aerial transport and deposition of dust produced in the chromate process and irrigation with tannery-contaminated water. Analysis of the impact of chromium in air and water on populations with various degrees of exposure revealed that highly harmful health effects were not observed. — Environ Health Perspect 103(Suppl 1):47–51 (1995)

Key words: chromium, pollution, exposure, León, groundwater, soil, aquifer

Introduction

Chromium is one of the metallic elements for which maximum concentrations in the environment are limited by the law due to its toxic properties. In nature it may exist in two oxidation states: (III) and (VI). The effects of chromium on health have been widely studied (*1–3*); Cr(VI) is about 300 times more toxic than Cr(III). Its impact on the environment also depends on the oxidation degree (*4,5*). Chromium compounds are used in many industries such as leather tanning, metal plating, and other metallurgical procedures. The inadequate disposal of their wastes may give rise to concentrations above the natural values.

In México the presence of chromium in the groundwaters used as a potable source for the city of León (one of the main urban and industrial centers of the country) was detected in 1975. As a result of a study carried out in León valley, the three main sources of the chromium in the groundwater were determined (*6,7*). Starting with the lowest contributor, weathering of pyroxenites (an ultramafic rock with a high total chromium content, around 1500 ppm) produced contamination levels in the range of 0.004 to 0.015 mg/l of Cr(VI), mainly to the northeast of the valley. Second, the practice of using residual ashes produced in brick manufacturing (containing more than 1000 ppm of hexavalent chromium) as fertilizer has polluted the widest area of the valley (around 180 km^2) and has generated chromium concentrations in the groundwater in the range of 0.005 to 0.04 mg/l. Finally, the inadequate solid waste disposal of the chromate factory Química Central (Qui Ce) in southwest León has produced the highest concentration levels—up to 50 mg/l—in the groundwater over a smaller area that measures about 5 km^2 (*7*).

The present study had the following objectives: *a*) to determine the extent and sources of groundwater pollution, *b*) to determine soil contamination patterns, *c*) to assess the impact on human health, and *d*) to assess the environmental impact in the area with highest chromium concentration levels within León valley in central México.

Materials and Methods

The effects of chromium on environment and population around a chromium compound factory (Qui Ce) were studied by monitoring water, soil, and human urine.

Water sampling was carried out in 30 wells and 5 piezometers 30 m deep located over an area of about 10 km^2 (Figure 1) as well as in the reservoir behind Qui Ce (San German dam). Concentrations of total and hexavalent chromium were determined in each sample. Hexavalent chromium was analyzed by colorimetry through its reaction with diphenyl-carbazide (*8*). After digestion with HCl and HNO_3, total chromium was determined by atomic absorption spectroscopy (*9*).

Soil sampling was performed in 56 sites, most of which were located in the corners of adjacent square cells (each side 200 m). In those sites where concentration anomalies were detected, 100 m^2 cells were used (Figure 1). Two samples of soil, each weighing 100 g, were obtained at each point: one sample from the surface soil and another from a 30-cm depth. For Cr(VI) extraction, 2.5 g of each previously quartered soil sample was added to 25 ml of distilled water, shaken for 2.5 hr and filtered. Cr(VI) was quantified in the filtrate by the same procedure used in water analysis. Total chromium concentrations were mesaured by dissolving 1 g of the quartered sample in a solution of concentrated HNO_3 and HCl, then analyzing it with an atomic absorption spectrophotometer.

Urine analyses were performed in samples obtained from four populations chosen on the basis of their exposure to chromium sources: group 1 consisted of 45 Qui Ce factory workers; group 2, 9 people living within a radius of about 500 m of Qui Ce; group 3, 6 workers of a tannery factory 3.5 km from Qui Ce, presumably exposed to Cr(III) only; and group 4, reference population from León and México cities (7 individuals), presumed not exposed to anomalous chromium sources.

Populations were classified according to the possible route of the contaminant (i.e., digestive or respiratory), length of exposure (i.e., seniority in the factory, or equivalent parameter), and by age, weight, and sex. Samples of urine accumulated over 24-hr periods were preserved with HNO_3.

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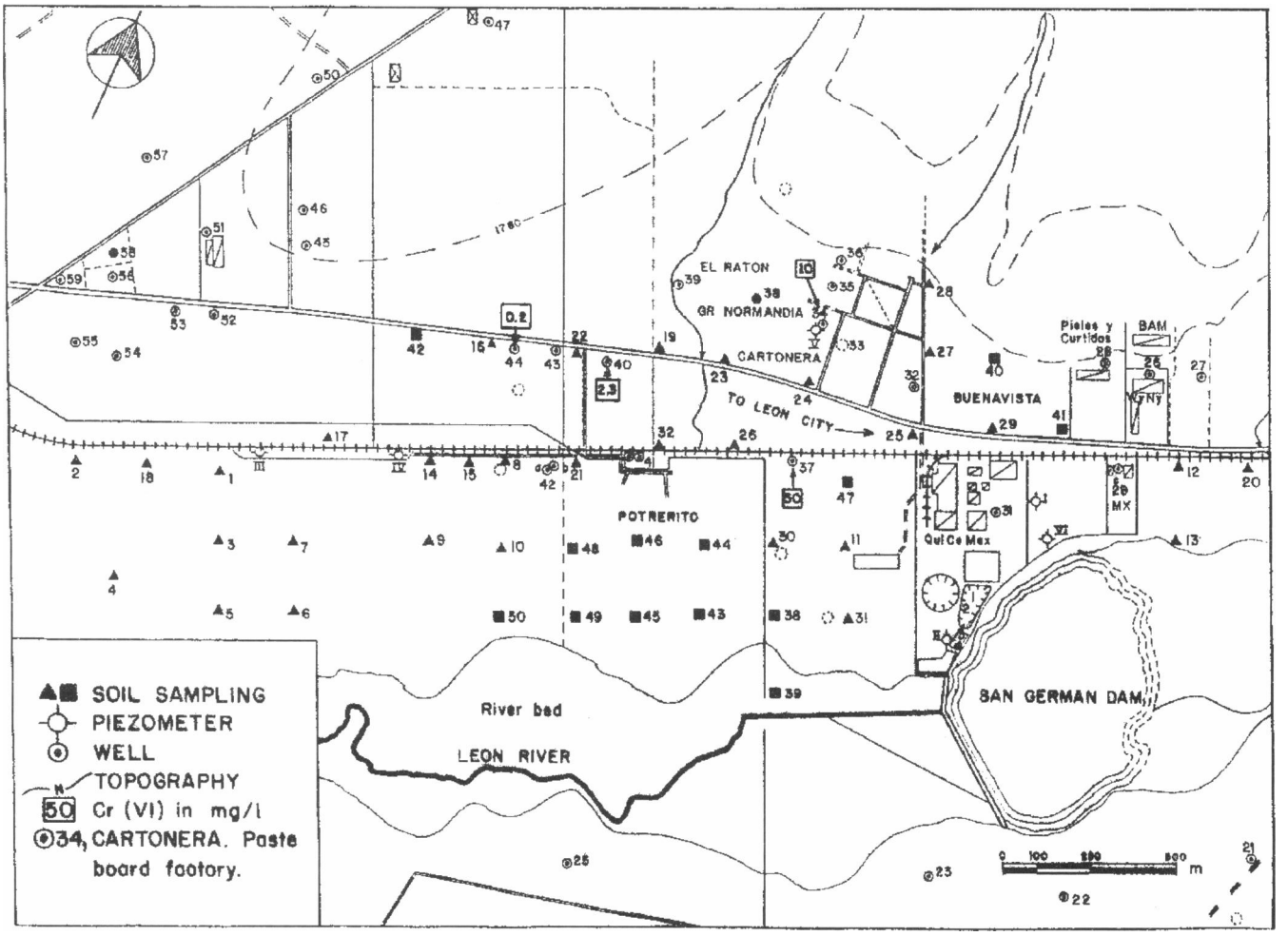

Figure 1. Sampling water and soil points.

Aliquots of 100 ml each were then evaporated to dryness and calcinated. This residue was dissolved in acidified water to a volume of 25 ml. Chromium concentrations were then determined by atomic absorption spectrometry.

Results and Discussion

Water Pollution

The extraction regime of the wells located around Qui Ce controls the extension of the pollution plume, which has kept a constant shape for the last 3 years, as shown by the results of the systematic monitoring of groundwater performed over that time.

The contamination plume has affected seven deep wells and six dug wells in an area of approximately 5 km^2, probably since the beginning of Qui Ce operation in 1970. Only one well in which water is currently used in the chromate factory process has shown Cr(VI) concentrations greater than 50 mg/l. This well (no. 37, Figure 1) is located near (about 300 m) the main point pollution source in that area, a disposal site of solid alumina residues containing an average of 6.12% (by weight) of hexavalent chromium and located in the factory yards (*7*).

In order of decreasing concentration, a value of 10 mg/l of Cr(VI) is found in a well (no. 34, Figure 1) the water of which is used by a pasteboard factory and a pig farm (Figure 1). The high rate of water extraction from this well seems to control the shape of the contamination plume, for its pressure head is at a higher altitude than the head of the chromate factory well and one would expect a different situation from the hydrologic recharge patterns. The waste water from the pasteboard process, with a high concentration of suspended solids, is disposed over the ground and mixed with the soil in the factory yards. Part of this land is used for drying pasteboard.

The remaining five contaminated wells (nos. 32, 40, 44, 42, 39, Figure 1) showed chromium concentrations between 0.05 and 2.3 mg/l. These wells seem to define a drawdown cone induced by water extraction (Figure 2).

All five piezometers were sampled at three depths. Measured chromium concentrations showed an inverse relationship with horizontal distance from the alumina disposal site of Qui Ce and defined the same contamination plume observed in the wells. Vertically, the maximum concentrations were found at a depth in the range 3 to 7 m below the water table and the presence of a more permeable layer. The lithology of the piezometer with the highest contamination (60 mg/l at 12 m depth) is shown in Figure 3.

The information obtained from the piezometers and from the sampled wells is not enough for an accurate determination of the tridimensional shape of the contamination plume. However, its vertical dimension may be estimated between 10 to 15 m, based on chemical results from deeper

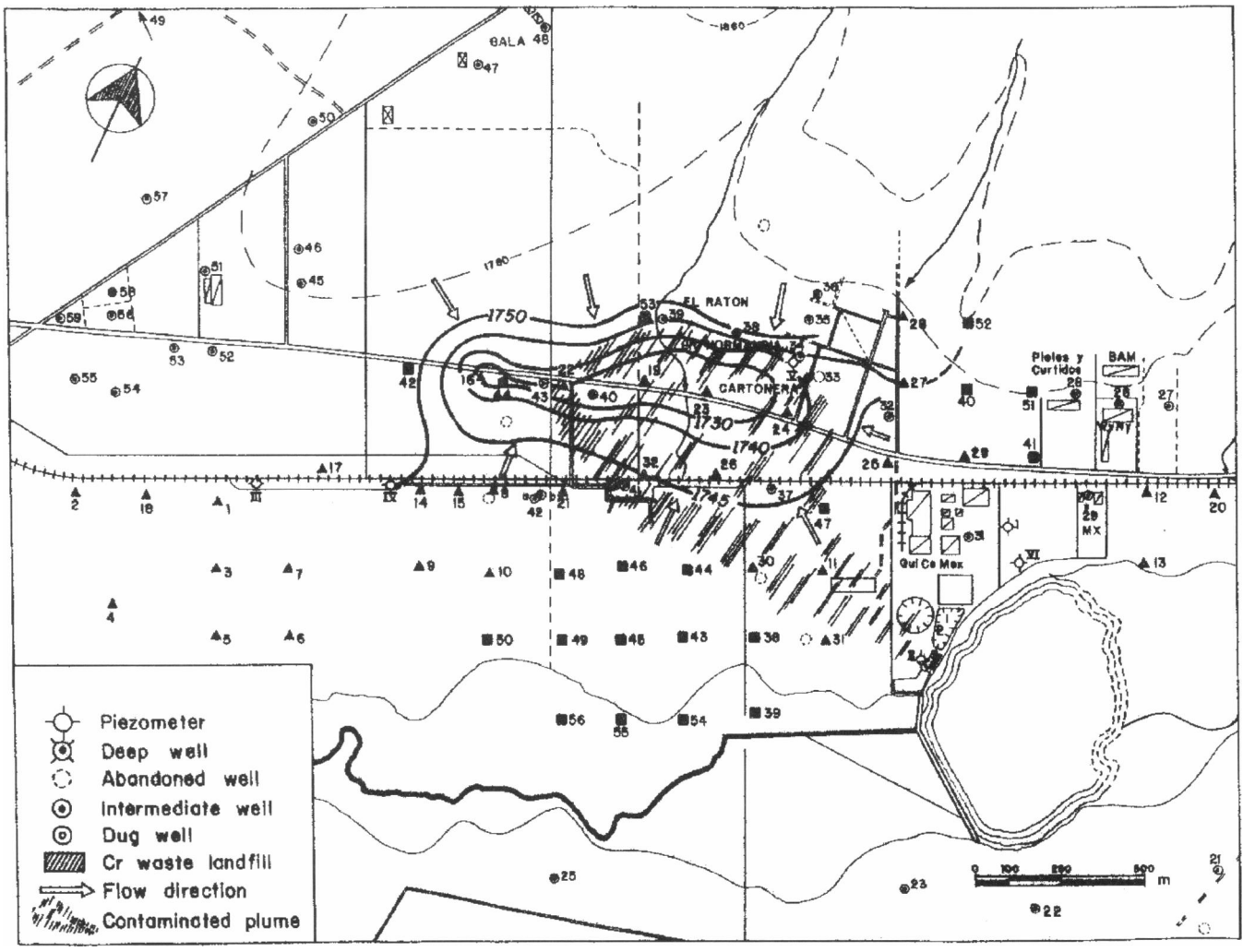

Figure 2. Pollution plume and local drawdown cone.

vertical water samplings. The well extraction regime favors horizontal flow toward the drawdown cone, making vertical flow less important and preventing the horizontal spreading of the contaminated volume in other directions.

An important superficial water body, the San German dam, is present in the study area (Figure 1). This body of water is very shallow (about 1 m average depth) and covers an area of approximately 0.5 km^2. It receives waste waters from two tanneries, Pieles y Curtidos and Wyny (Figure 1). Because of this practice, Cr(VI) has reached an average value of 0.004 mg/l, and total chromium concentration of 0.144 mg/l. The dam's water is used for irrigation in the nearby lands. Surprisingly, neither the dam nor the irrigation practice has a significant role in the contamination of the groundwater or its flow (*10*).

Soil Pollution

Hexavalent chromium in soils was detected only in 11 superficial and 12 deeper samples, with values ranging from 0.020 to 1.72 ppm (dry basis). The highest Cr(VI) values were located in front of Qui Ce about 10 m from the entrance (points 25 and 29, Figure 4). The presence of chromium in those sites may have been caused by inadequate handling of the chromate products in their transport outside the factory. Some sampled points had Cr(VI) concentrations greater at the surface and others greater at a depth of 30 cm. This may be explained by assuming the presence of chromium is a result of a superficial deposition of a solid chromate compound; the concentration differences observed between the two sampled depths may then depend on the porosity, on the adsorption capacity of each layer, or on the absorption by the prevailing vegetation (*11*).

Total chromium distribution for the superficial samples is shown in Figure 4. The higher values of 1000 ppm (dry basis) cover an area of about 0.125 km^2 northwest of Qui Ce, near sampling point 47. From there, concentrations decrease in irregular ways. This global concentration behavior may be attributed to the transport of the chromium dust emitted at Qui Ce by the predominant winds (SW–NE). The dust is produced mainly in the grinding and calcination of the chromite, and although electrostatic precipitators are used for removing the chromium dust, their operation is recent (since 1989). Several smaller local maxima (near points 52, 54, 13, Figure 4) were also detected. Chromium concentrations in these areas may originate from different specific sources, namely, the disposal of leather residues over the ground and the irrigation with the San German dam water and also with tannery waste water. Total chromium concentration for

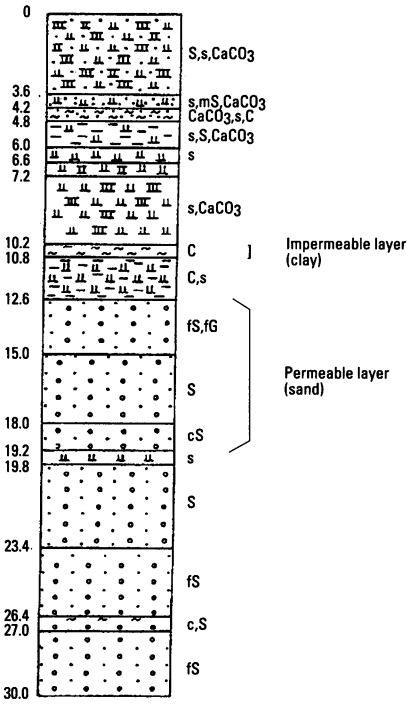

Figure 3. Lithology of the most contaminated piezometer. S, sand; s, silt; C, clay; f, fine; m, medium; c, coarse.

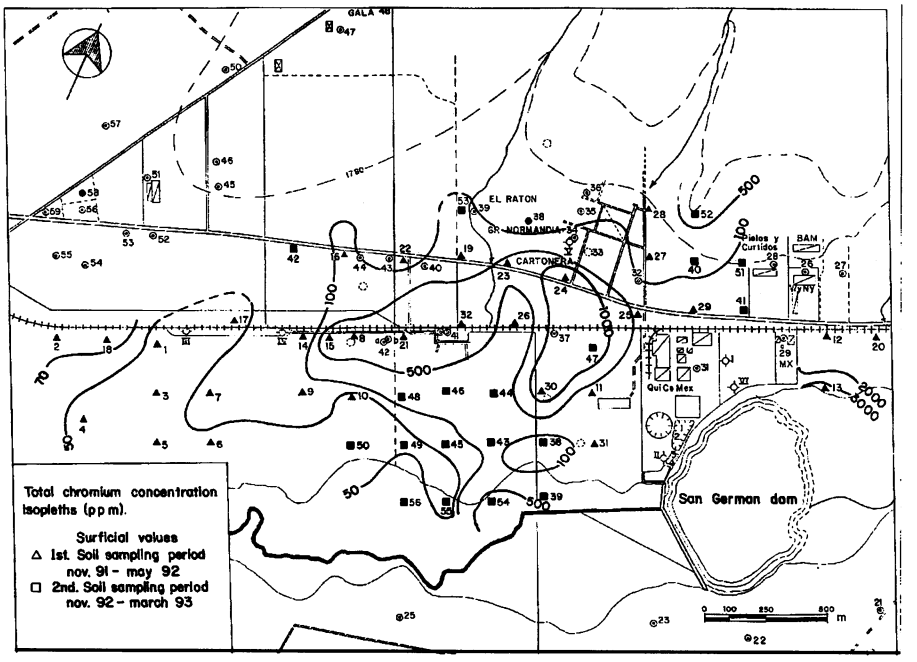

Figure 4. Total chromium concentrations (ppm) in soils for the superficial samples.

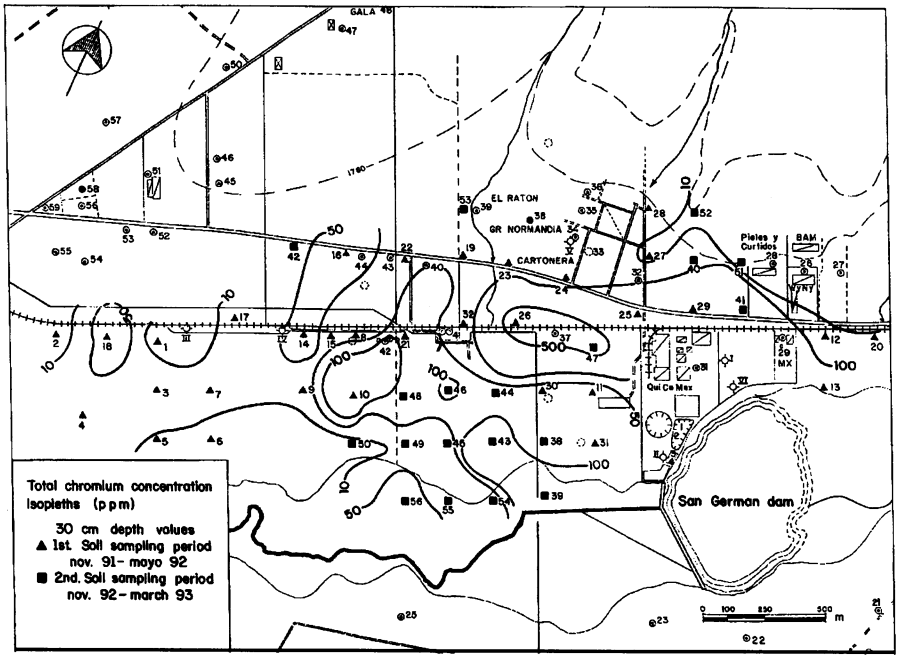

Figure 5. Total chromium concentrations (ppm) in soils for the 30-cm depth samples.

the samples obtained at a 30-cm depth is shown in Figure 5. Although the distribution pattern for 30-cm depths is not the same as for surficial soils, the higher values for both depths are located in the same areas. The concentration differences may be due to evaporation, adsorption, absorption by plant roots, and percolation through fractures or layers, with various permeabilities distributed in irregular patterns.

Health Effects

Chromium concentration in urine has been used for biological monitoring of human exposure to chromium compounds (*12,13*). Correlations between chromium content and health effects are difficult to establish, particularly when the levels of exposure are not very high. Maximum allowances for chromium are 0.05 mg/l in water (World Health Organization) and 0.025 mg/m^3 time-weighted average in air (National Institute for Occupational Safety and Health). The major health effects researched in this study were nasal septum perforation, lung cancer, and birth deffects.

Two routes of exposure to chromium compounds were analyzed, namely, air (Qui Ce workers exposed to chromium dust in the air), and water (people living near Qui Ce exposed mainly to chromium in the water). Air concentrations measured at the office and factory utilities were lower than 0.025 mg/m^3.

Some of the population living around the factory consumed water contaminated with Cr(VI) at concentrations as high as 0.5 mg/l for periods of 5 to 7 years. Consuming water with higher chromium levels did not occur because of the yellowish color it acquires when concentrations rise above 0.5 mg/l.

In the present study an average global concentration of 27.29 ± 28.0 ng/ml of chromium in urine was determined for all the sampled populations (a total of 68 individuals); an average value of 20.03 ± 8.8 ng/ml was found for the reference group.

Urine concentration was higher for Qui Ce workers with 33.23 ± 33.1 ng/ml. Values of chromium in urine above 120 ng/ml are considered critical (*14*). In the population living around Qui Ce, adverse health effects were not detected as a result of drinking contaminated water, nor was chromium accumulation with the time of exposure determined from the beginning of Qui Ce operation in 1971. The average concentration in urine for this population (nine individuals) was 26.25 ± 4.5 ng/ml.

Within Qui Ce the population was divided into three groups (clerks, factory workers, and laboratory technicians). The average concentrations found in urine were, respectively: 31.72 ± 23.2ng/ml for eight individuals, 46.79 ± 36.9 ng/ml for 34 individuals and 21.20 ± 10.1 ng/ml SD for three individuals. Within the factory worker group, no correlation could be established between chromium content and seniority or labor area. Since the beginning of the factory operation, only 17 of 700 workers have presented nasal septum perforation without any further consequences. In the same period no cases of lung cancer have been detected. The incidence of birth defects for 28 women working at least 6 months during their pregnacy in Qui Ce (in the laboratory and office) was checked and none were found. Tannery workers showed average chromium concentration in urine of 19.16 ng/ml, which was less than the global value of 27.29 ng/ml.

Personal communication from the pig farmer indicated that no significant health effects have been observed in the animals that drink only chromium-contaminated water with an average Cr(VI) concentration of 10.0 mg/l.

Conclusions

Highest values of Cr(VI) contamination in groundwater were found in a small area around the chromium compound factory. From the high solubility of this oxidation state of chromium, it was expected that this contamination plume would extend over a more extensive area. However, the high rate of water extraction in nearby wells changed the underground water circulation patterns containing the plume. Highly contaminated surface water has affected the soil rather than the groundwater around San German dam. This is probably due to the combined effect of an impermeable layer covering the bottom of the dam and the low solubility of Cr(III), the main contaminant present in that lake.

Chromium presence in soil at levels higher than the regionally observed values (less than 30 ppm) is attributed mainly to the aerial transport of chromium dust emitted by Qui Ce and, to a lesser extent, irrigation with contaminated waters from the San German dam.

Exposure of people living around the factory or working in it has been mainly to chromium compounds in the air or in the groundwater. Chromium concentrations in urine were greater for individuals exposed to chromium in air. The highest average concentrations of chromium in urine were found in Qui Ce factory workers. Neverthless, there was no evidence of important health effects that could be directly attributed to chromium-in-air exposure contrary to that expected from such a route.

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